UNIVERSITY COAL RESEARCH/HISTORICALLY BLACK COLLEGES AND UNIVERSITIES AND OTHER MINORITY INSTITUTIONS CONFERENCE, NETL/DOE, Pittsburgh, PA, June 2-3, 2010

Project Title: Development of Novel Ceramic Nanofilm-Fiber integrated Optical Sensors for Rapid Detection of Coal Derived Synthesis Gas

Grant #: DE-NT0008062

Project Duration: 04/01/2009 – 03/31/2012

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Outline of Presentation

1. Objective and Schedule
2. Concepts of Fiber Optic Sensors
   - Proposed two types of FOS
   - Material development
3. Research Progress
   - Development of fiber device
   - Materials research
4. Summary of Work Done
5. Work Plans for Year-2

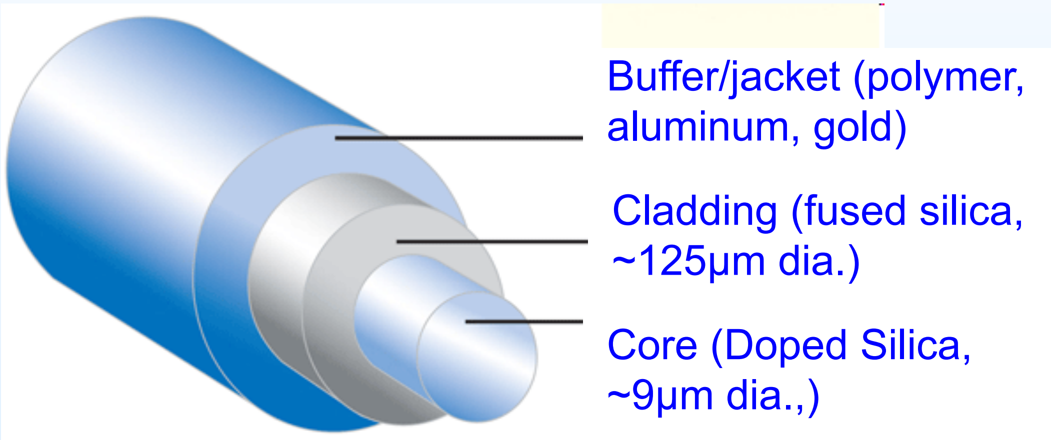
Appendix: Publications

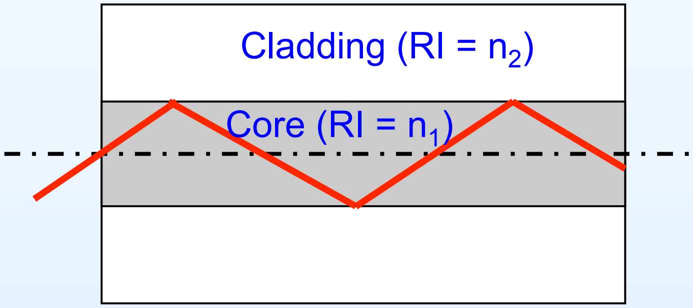
1. Project Objective and Schedule

- **Project Objective :**
  - To investigate and demonstrate nanocrystalline doped-ceramic coated fiber optic sensors (FOS) for rapid gas detection in syngas streams and combustion gases.
  - To develop sensors and sensor materials for H_2, CO and H_2S detection at >500°C and pressure up to 250 Psi.
- Research schedule:
  - ***Year 1:*** Model design of the LPFG-coupled interferometer and evanescent tunneling fiber sensors; development of nanocrystalline doped-ceramic materials suitable for gas sensing
  - ***Year 2:*** Sensor fabrication (including integration of the nanofilm with fiber devices) and improvement of the ceramic nanofilm properties and fiber structures for enhancing sensor performance
  - ***Year 3:*** Evaluation of sensor performance in multicomponent gas mixtures under temperatures >500°C and pressures up to 250 psi.

Optical Fiber Sensor

- **Optical fiber: A light pipe made of fused silica materials**

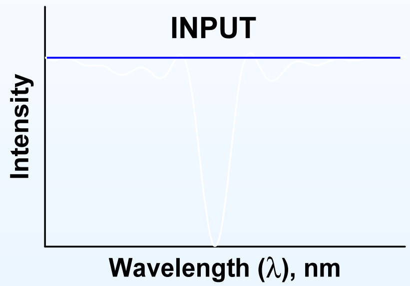


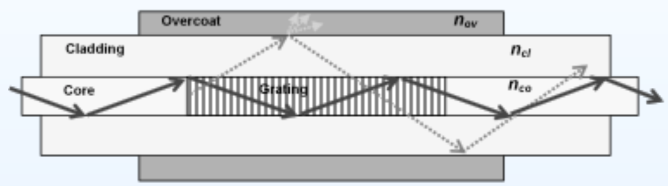


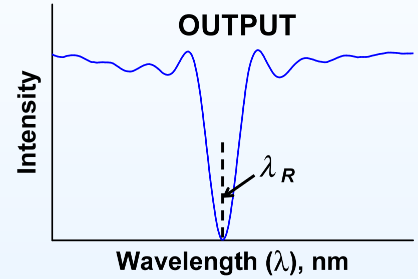
Light guiding via total internal reflection at the core-cladding interface

- **Fiber sensors: proven advantages for various applications**
  - Small size/lightweight
  - Immunity to electromagnetic interference (EMI)
  - Resistance to chemical corrosion
  - High temperature capability
  - High sensitivity
  - Remote operation
  - Multiplexing and distributed sensing

2. Concept of Nanofilm-Fiber Optical Gas Sensor







Mechanism:

$$\lambda_R = (n_{eff} - n_{clad})\Lambda$$

$$\frac{d\lambda_R}{dn_{ov}} = \frac{d\lambda_R}{dn_{cl,eff}} \frac{dn_{cl,eff}}{dn_{ov}}$$

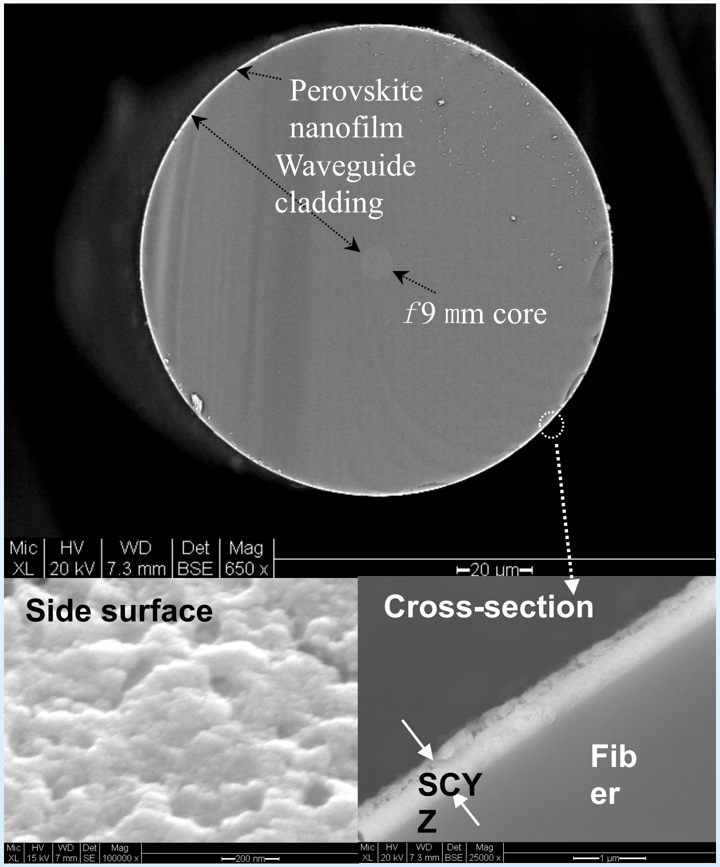
$Dl_R = f(n_{ov})$ where $n_{ov} = g(p_{gas}, T)$

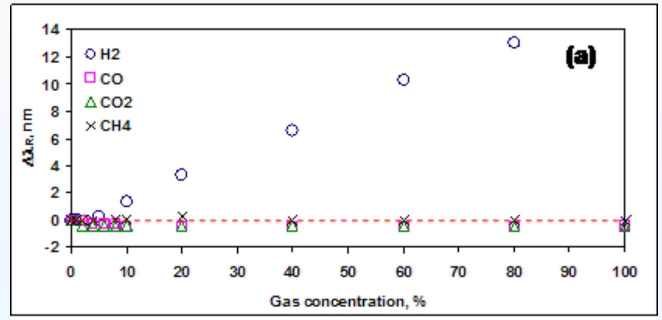
Therefore, Dl_R represents gas concentration at a fix temperature

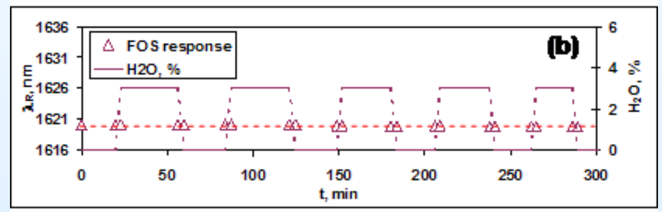
- **EXAMPLE: Nanocrystalline doped ceramic coated long period fiber grating (LPFG)**
  - **Device:** resonance wavelength of LPFG is very sensitive to environmental refractive index change
  - **Mechanism:** chemical sorption or gas-solid reaction induced refractive index changes (Δn) of the coated ceramic thin film
  - **Detection:** Shift in the resonance wavelength (Δλ) of LPFG

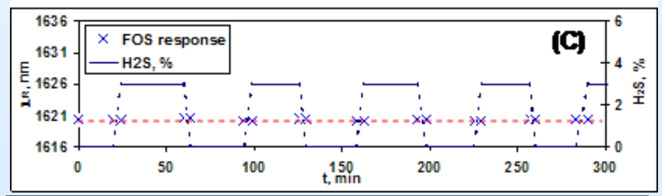
Previous Results:

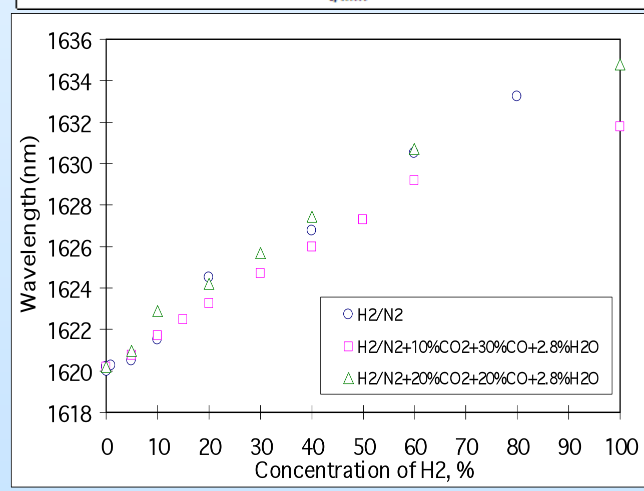
$Sr(Ce_{1-x}Zr_x)_{0.9}Y_{0.1}O_{3-\delta}$(SCZY) thin film for H_2 sensing









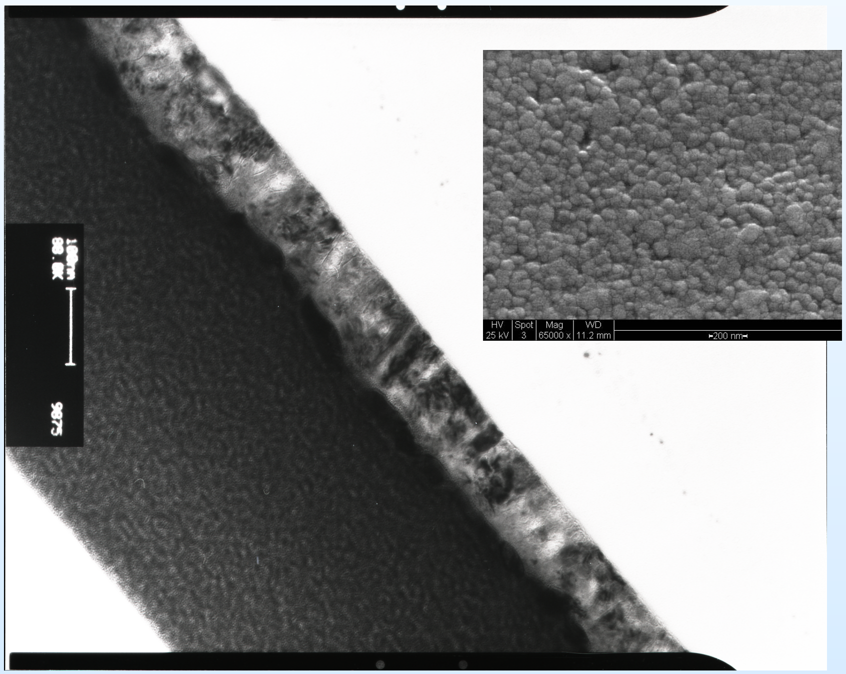


SCZY-LPFG showed high selectivity, good sensitivity, and reasonable response time at 500°C and 1 atm; thermal drifting of signal is a concern.

Previous Results

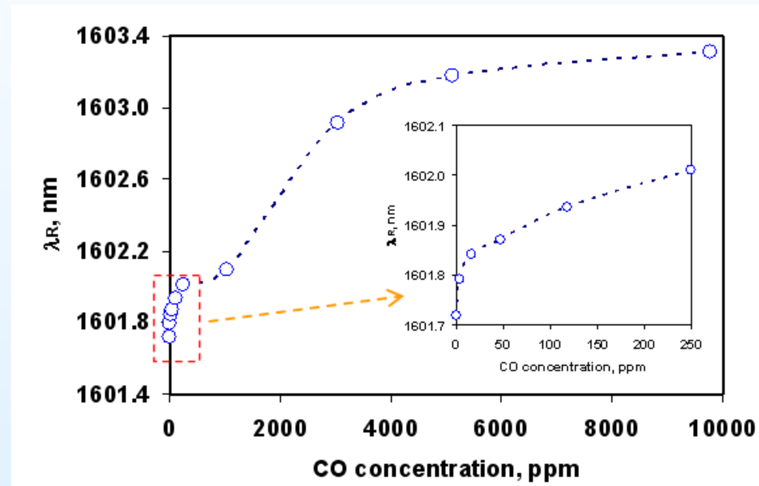
Copper-doped zirconia (CDZ) Coating on LPFG for CO Sensing

Nanocrystalline $Cu_{0.16}Zr_{0.84}O_{1.84}$ thin film on optical fiber

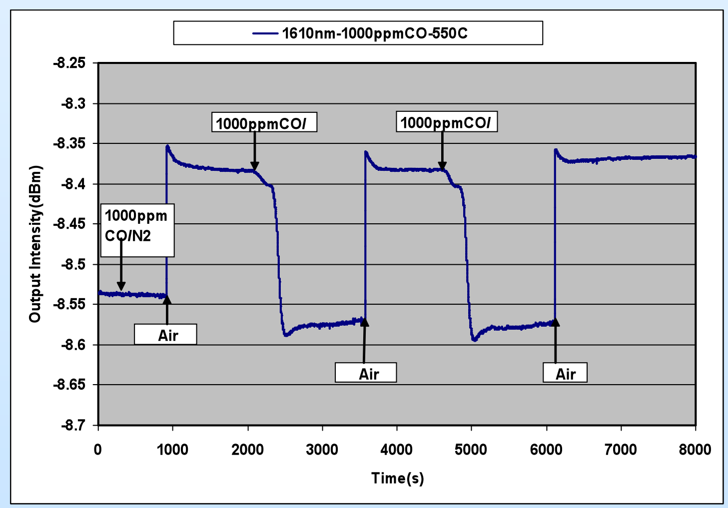


16%Cu CDZ-LPFG showed high good sensitivity and fast response to CO at 550°C and 1 atm; thermal drifting of signal and CDZ chemical instability in high concentration of CO are major concerns.

Response to CO concentration



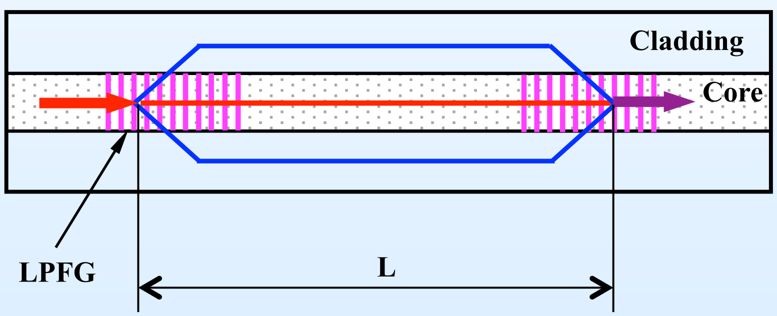
Sensor reversibility and response speed

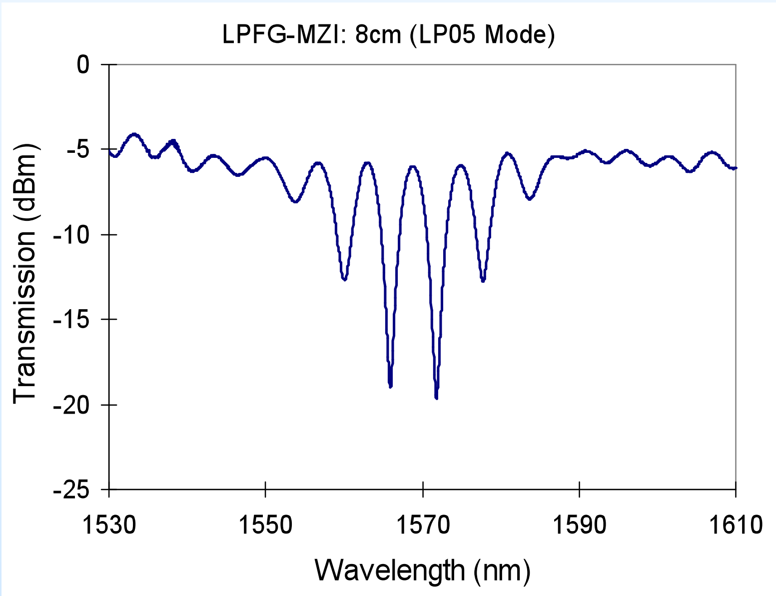


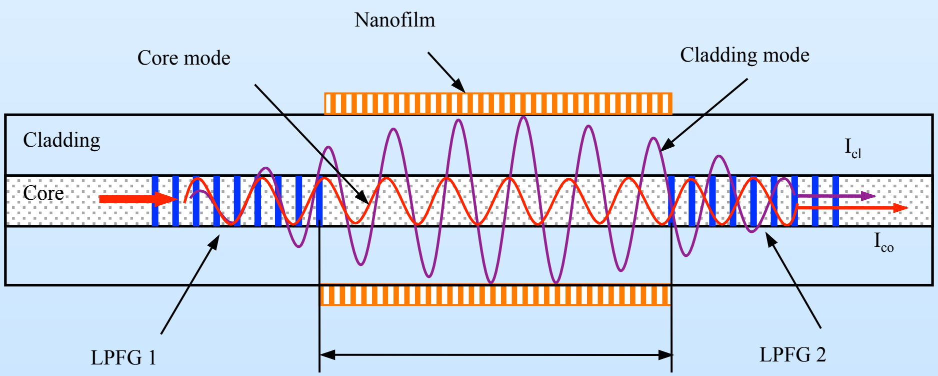
2.1 Two Types of FOS Proposed in This Project

1) Mach-Zehnder (MZI) and Michelson interferometers (MI)

- LPFG coupling light from core to cladding
- Core-cladding mode interference
- High-T capability and self-compensation for temperature drift

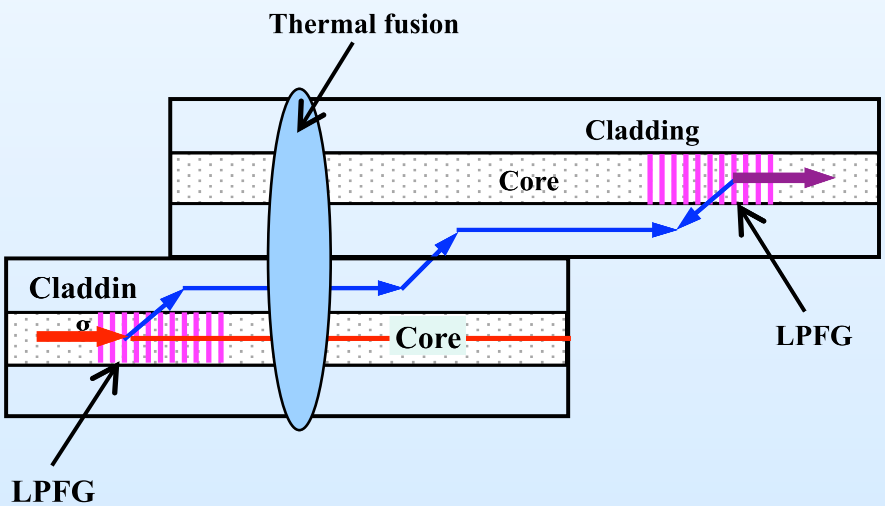


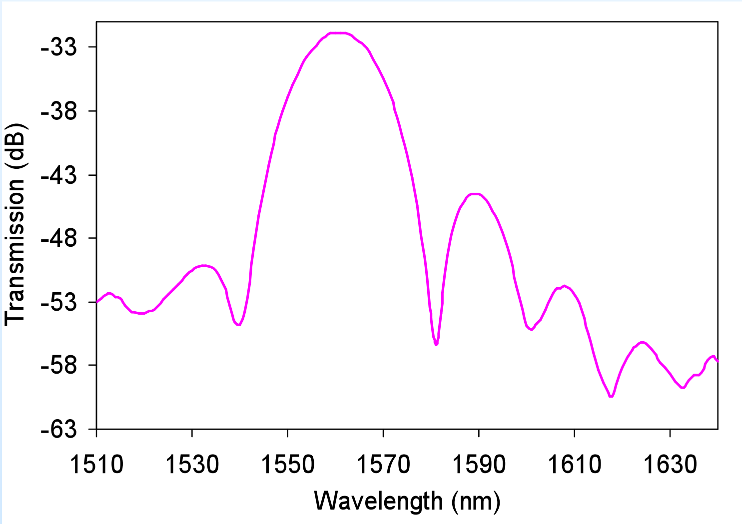




2) Cladding Tunneling LPFG Pair

- **Tunneling through two LPFGs fusion spliced together**
  - Extremely high sensitivity to refractive index change
  - High-T capability; Self-compensation for temperature drift





2.2 Development of Sensing Materials

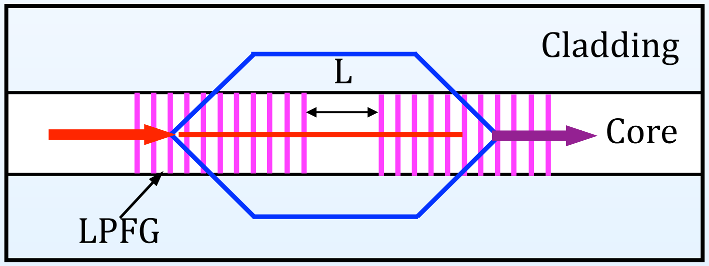
- Proton Conducting Perovskite Oxides (for H2 detection)
- Copper-Doped Zirconia (CDZ; for CO detection)
- Characterization of Materials and test LPFG-based sensors
- Application of Selected Materials to the Two Types of Fiber Devices (to be performed in project year 2)

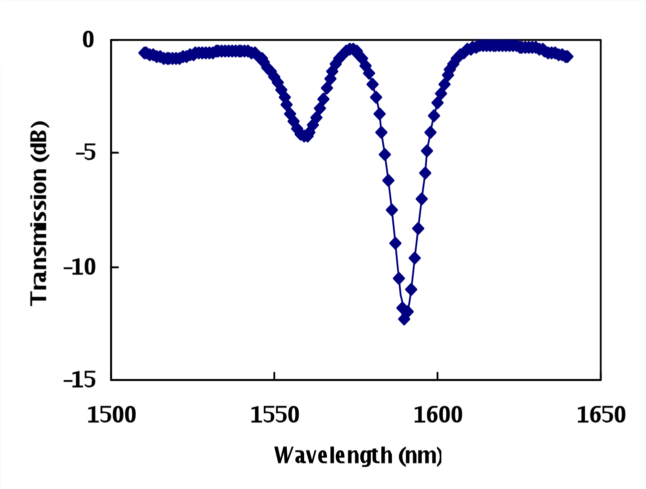
3. Research Progresses in Year 1

- Model-based design of fiber sensor devices
- Materials development and characterizations

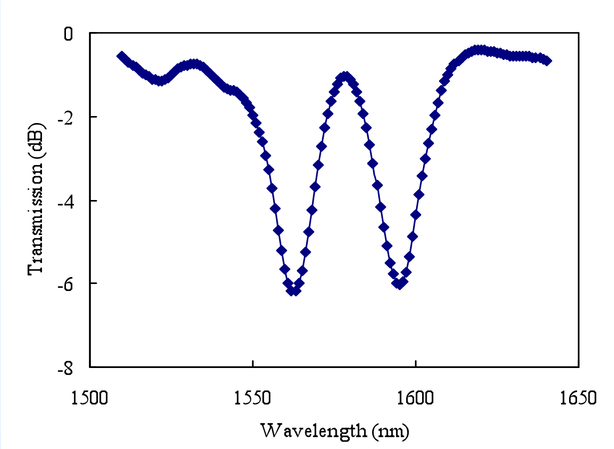
3.1 Design and Fabrication of Fiber devices

Type 1 – In line interferometer (two-section)

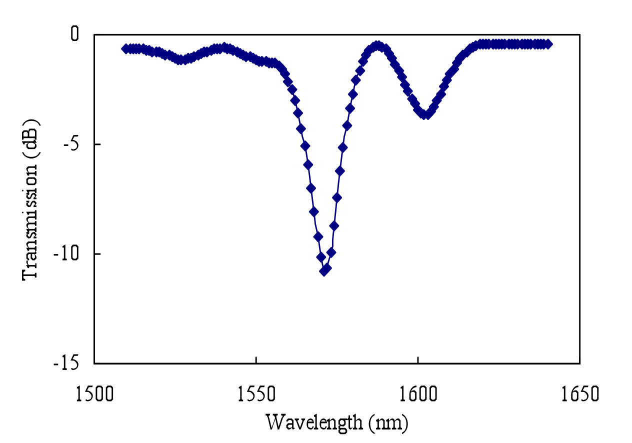




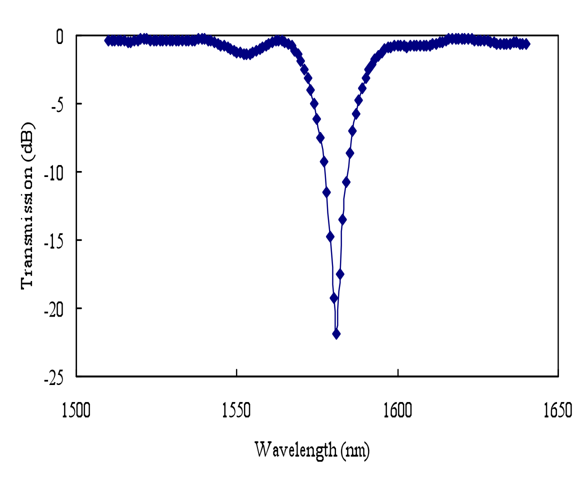
L= 1/4 period



L= 1/2 period

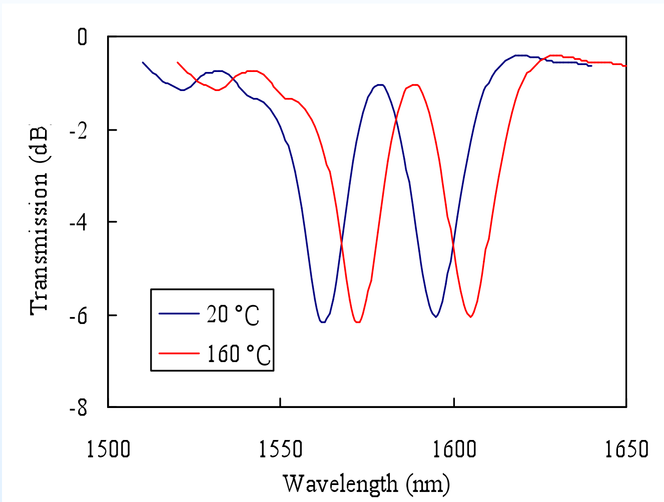


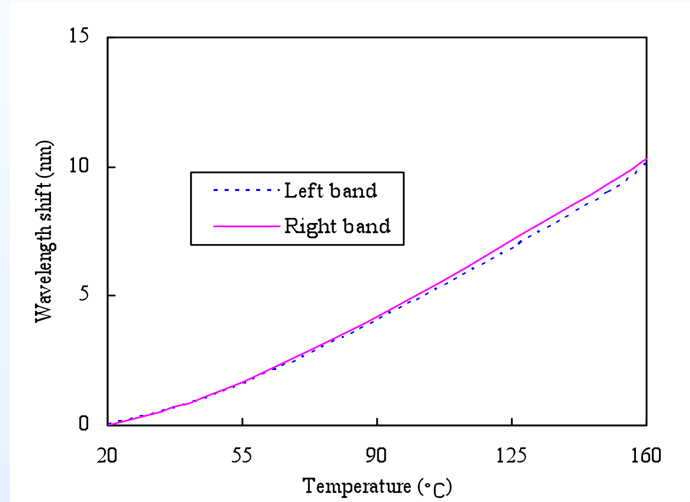
L= 3/4 period

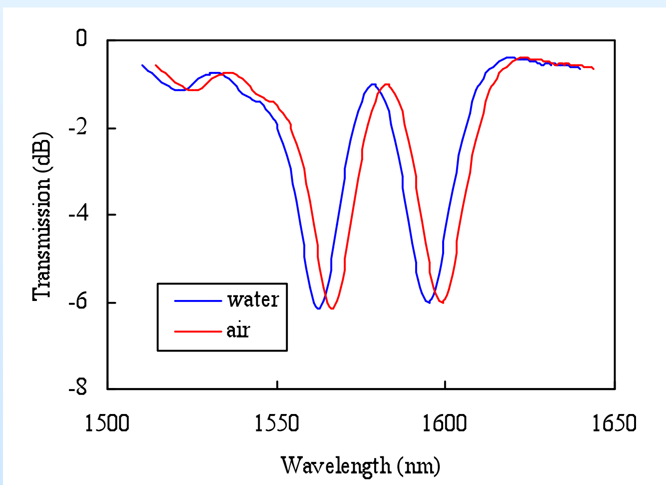


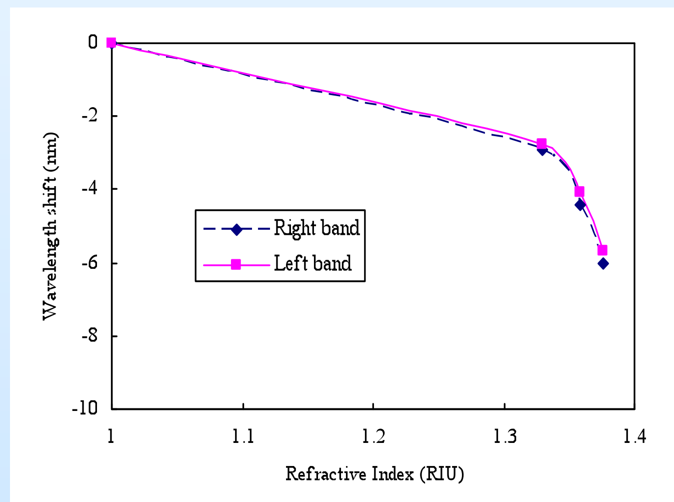
L= 1 period

Temperature and RI responses





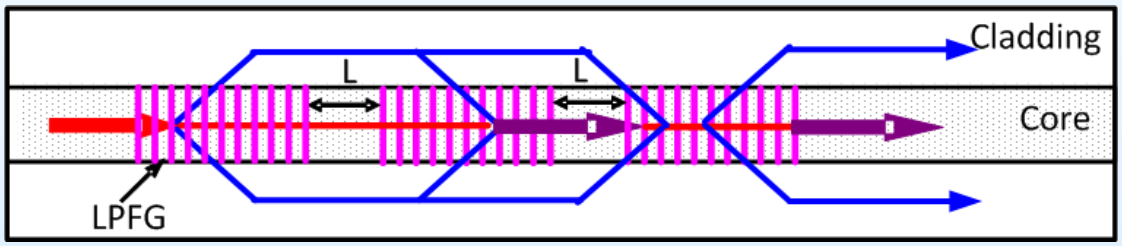


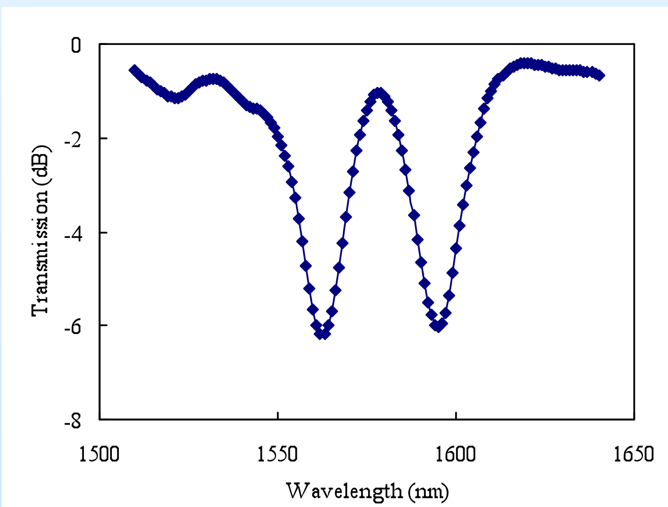


- Two bands have almost the same responsivity towards temperature and refractive index

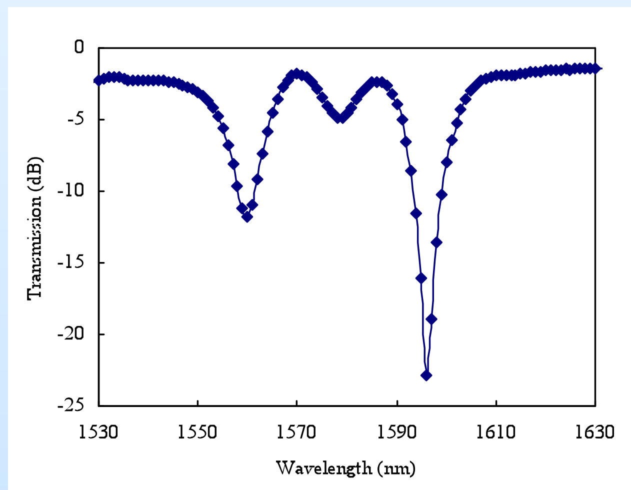
Three-Section Device

- Light re-coupling/re-mixing through the third section.
- The resonant wavelength will change because of third section of LPFG. What happen if we add another section of LPFG (the three-section PS-LPFG)?





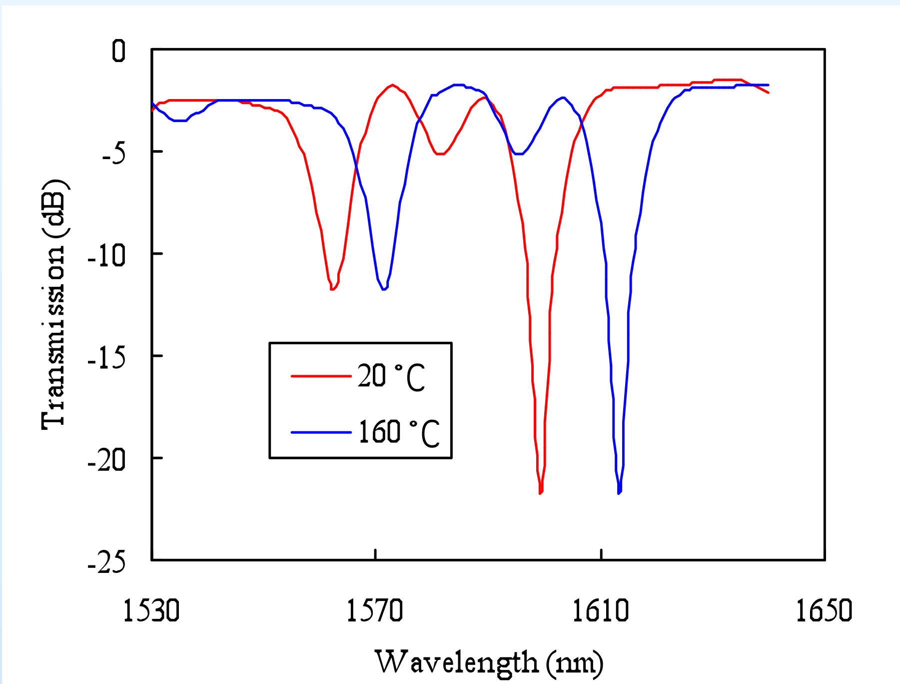
Two-section, L = 1/2 period

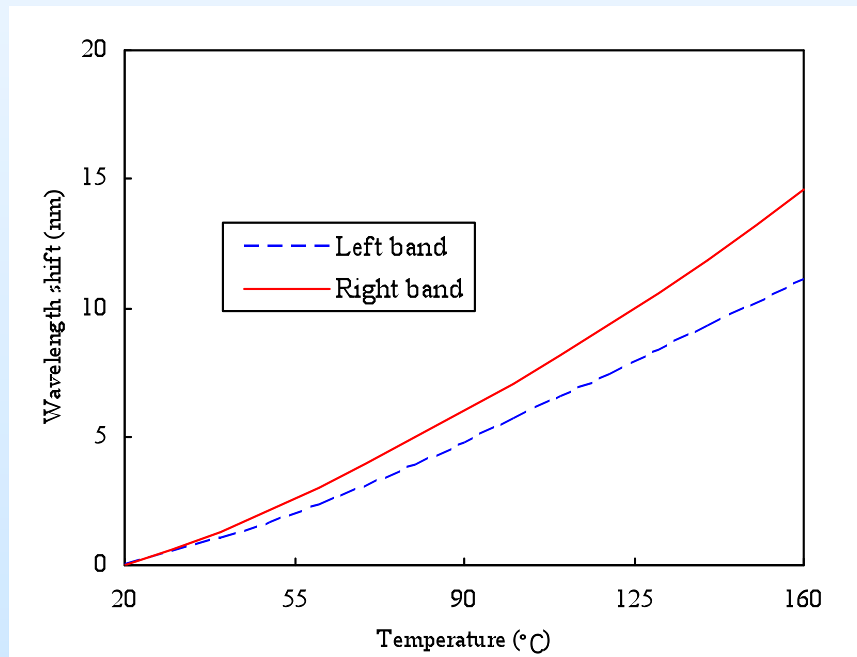


Three-section, L = 1/2 period

Temperature Sensitivity of Three-Section

- Two attenuation bands shifted to the long wavelength as temperature increased.
- The right (red) band had a higher temperature sensitivity than the left (blue) band

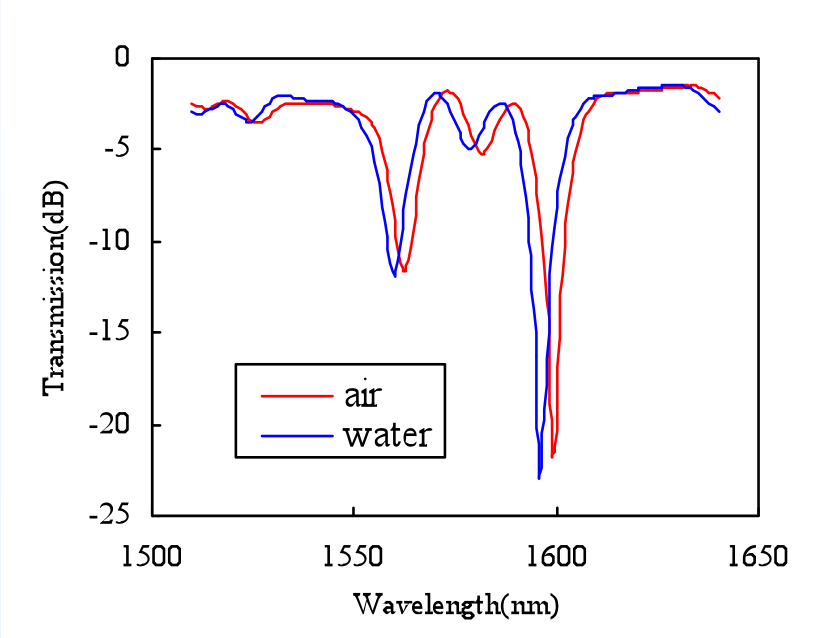


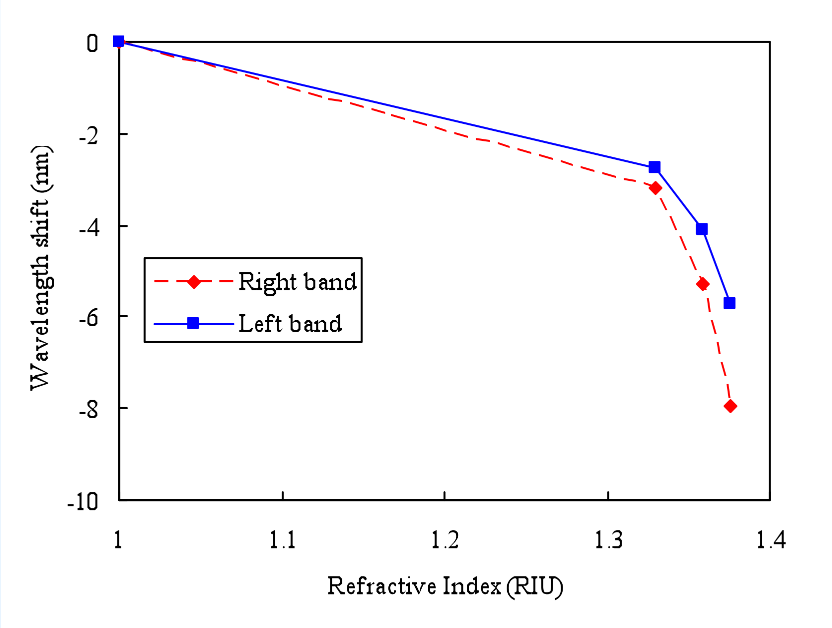


Center wavelength shift of two bands of 5th order Three-Section PS-LPFG versus temperature

RI Sensitivity of Three-Section PS-LPFG

- The right (red) band has higher refractive index sensitivity than the left (blue) band.
- It is possible to use a three-section PS-LPFG for multiparameter measurement

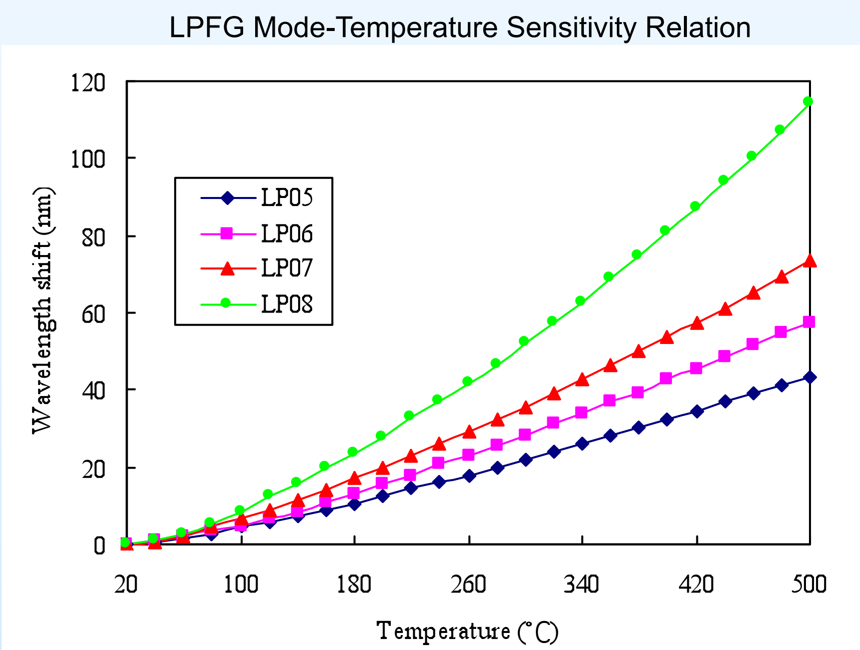


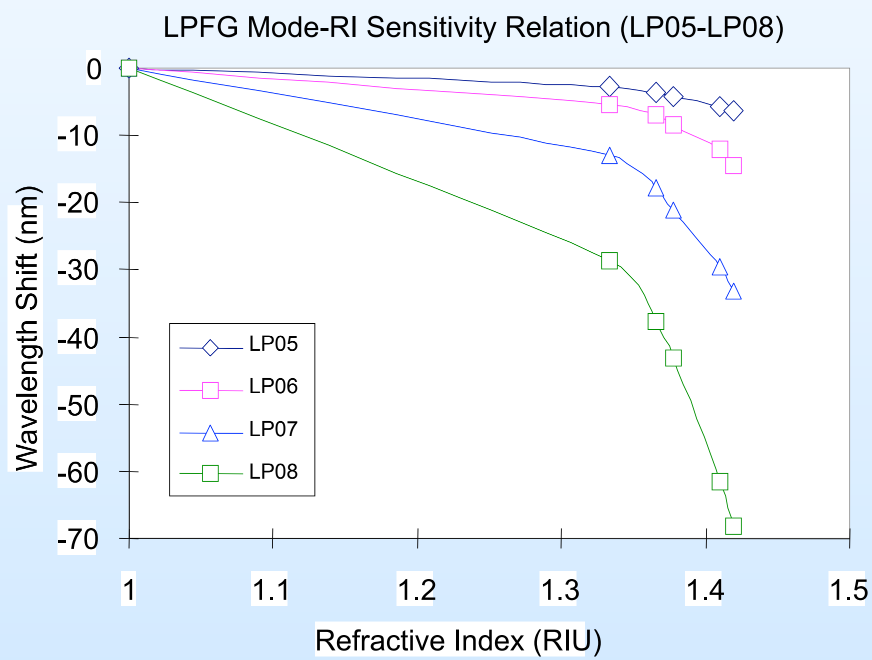


Center wavelength shift of two bands of 5th order Three-Section PS-LPFG versus refractive index

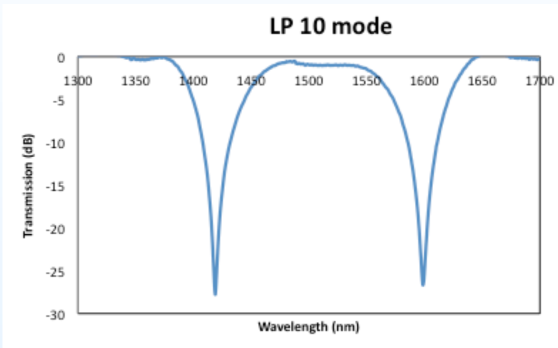
Mode Dependent Sensitivity

- Different cladding mode LPFG has different sensitivity to temperature and refractive index.

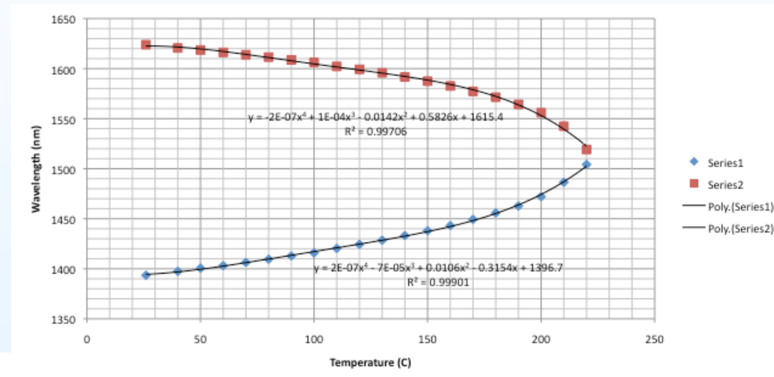


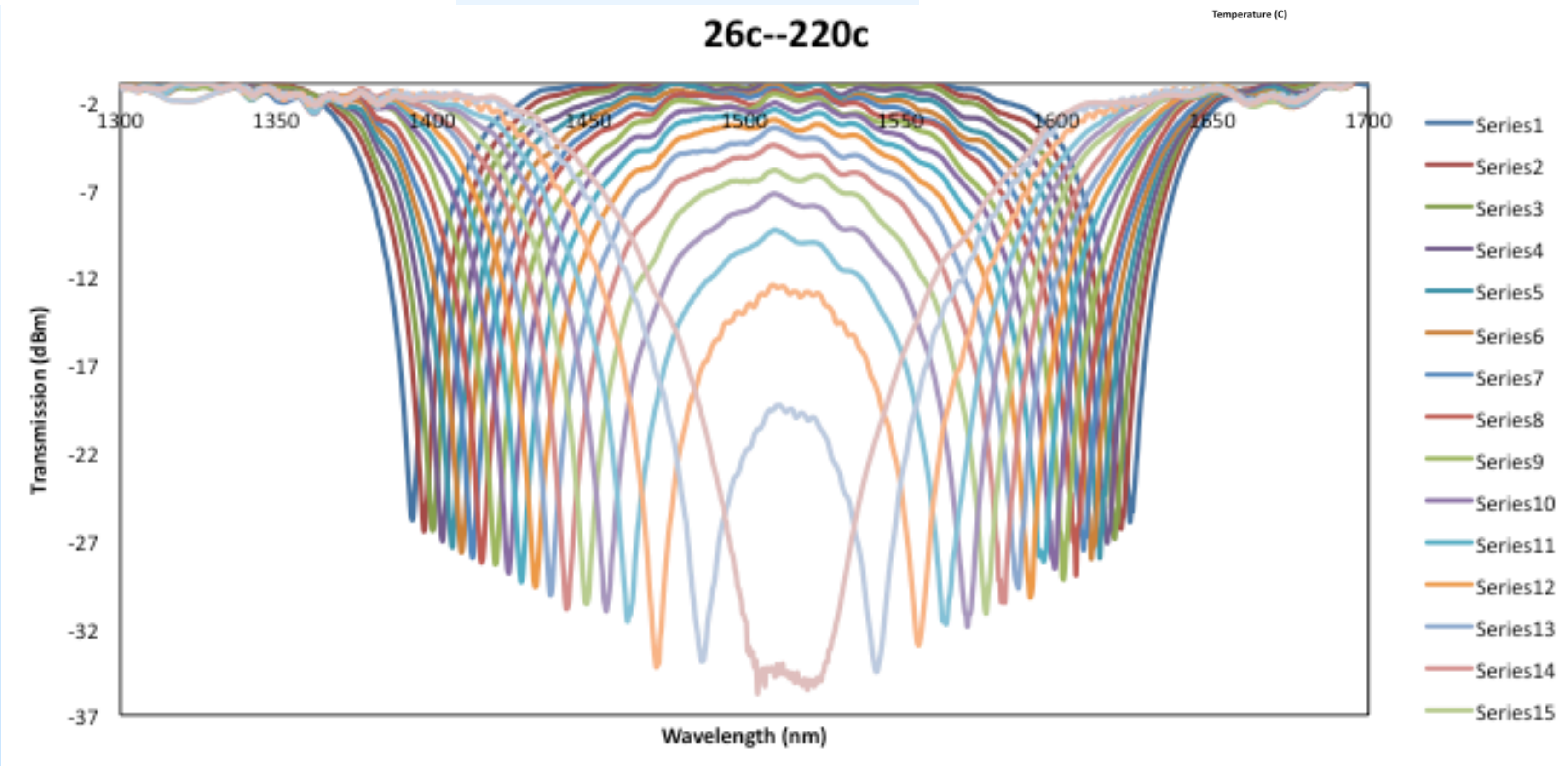


10th Order Mode LPFG



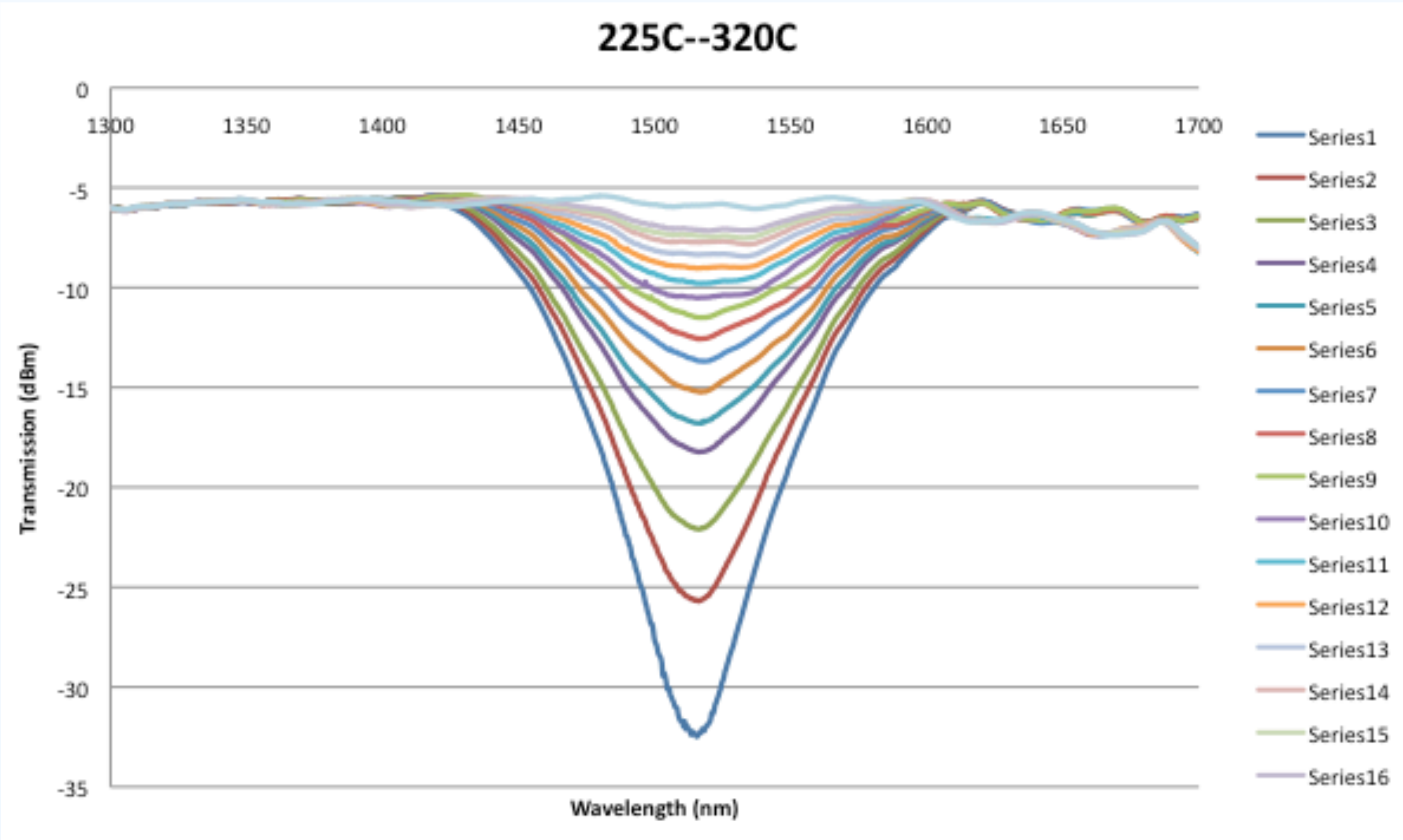
- Split
- > 220C?





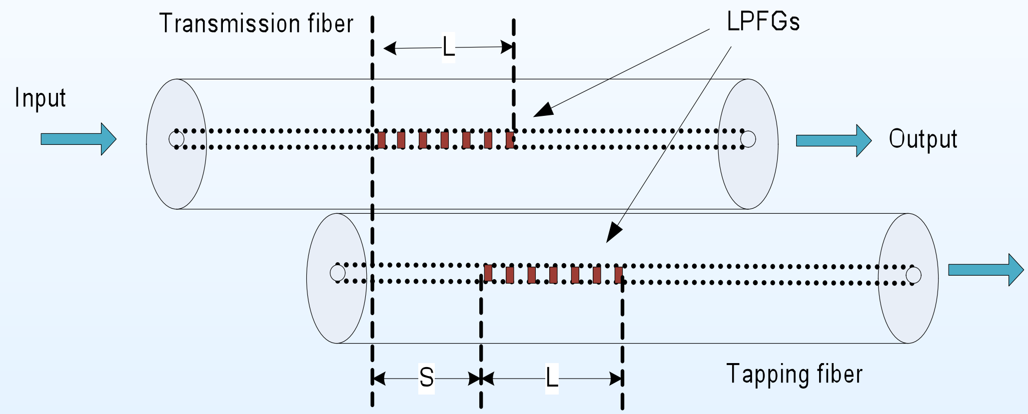
Turning Point Device

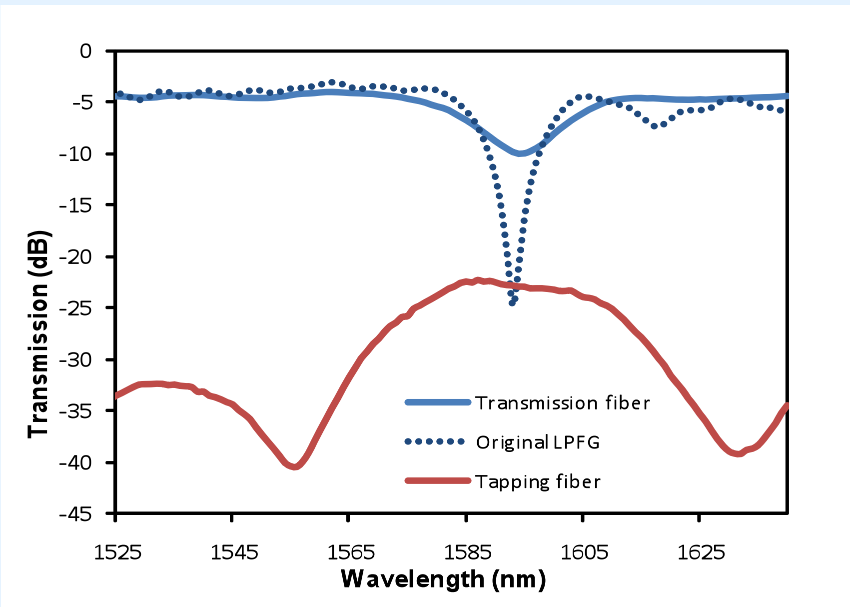
- >220C, no spectral shift, intensity changes only



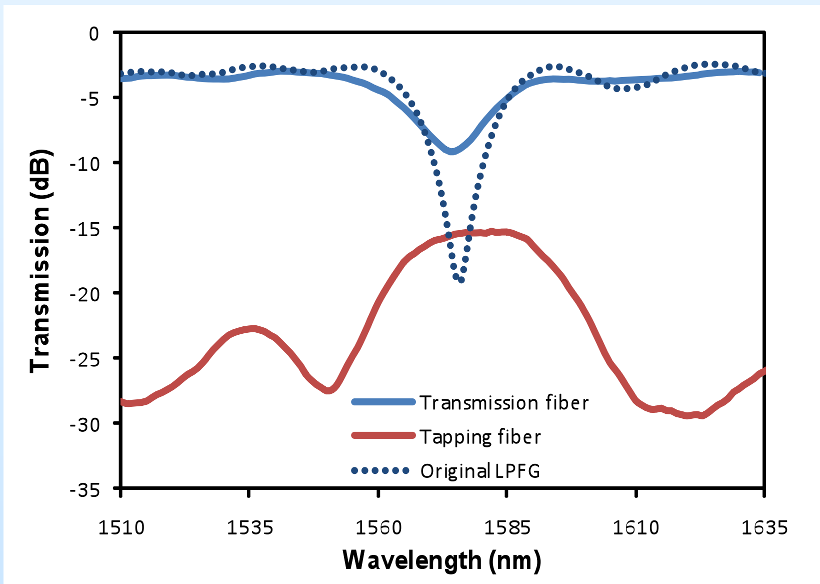
Type 2 – Side Coupled Devices

- Side coupled LPFG pair



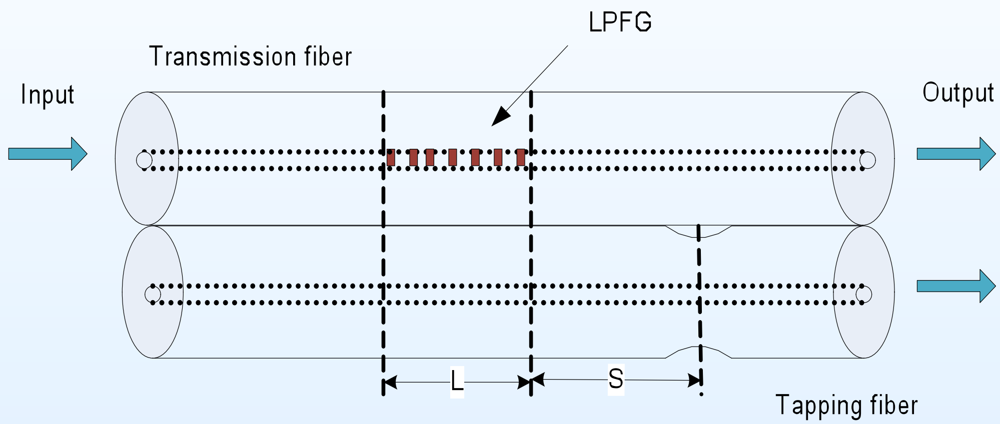


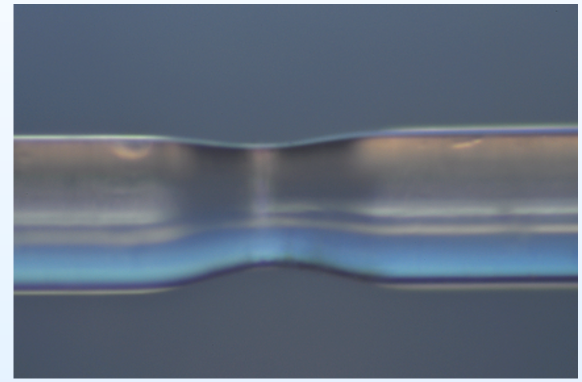
LP05 Pair

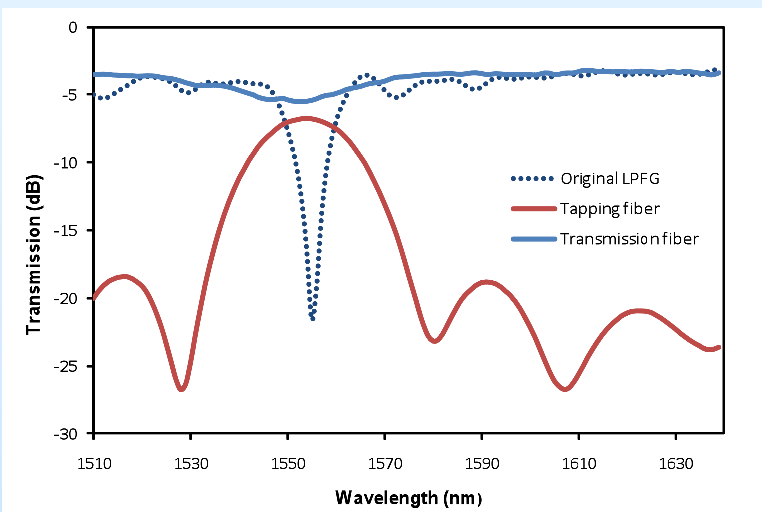


LP06 Pair

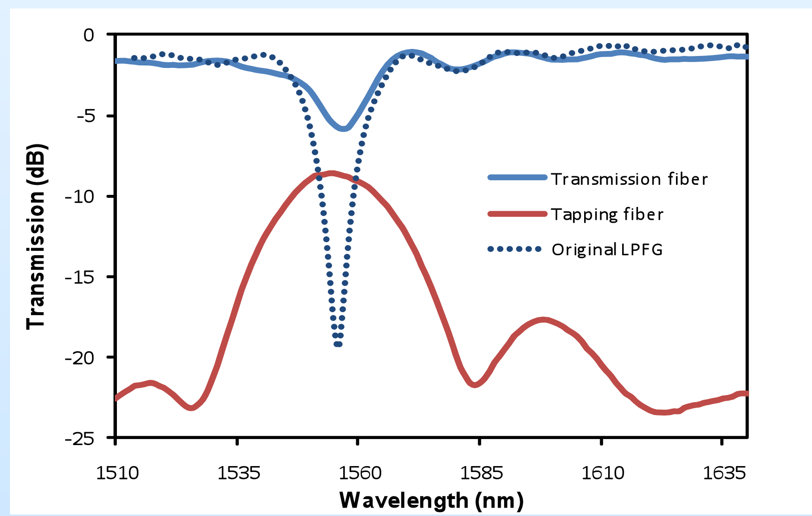
Side Coupled LPFG-Taper





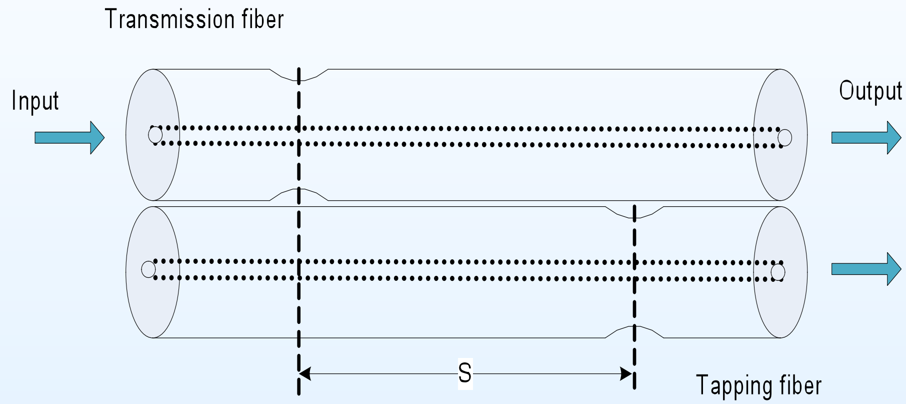


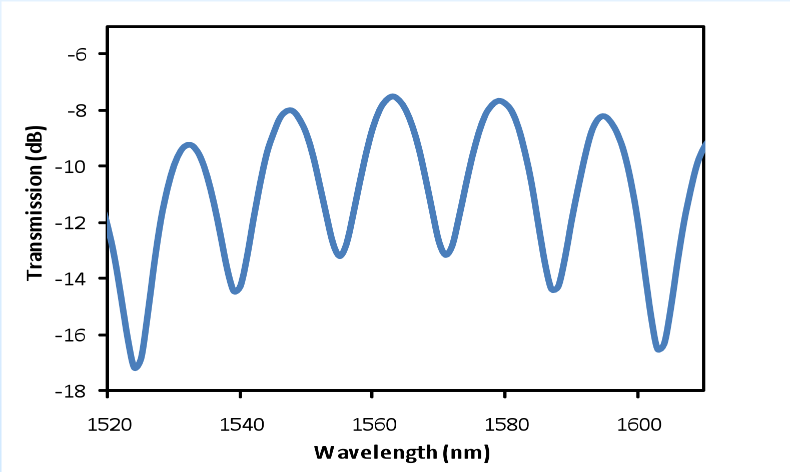
LP05-Taper Coupler

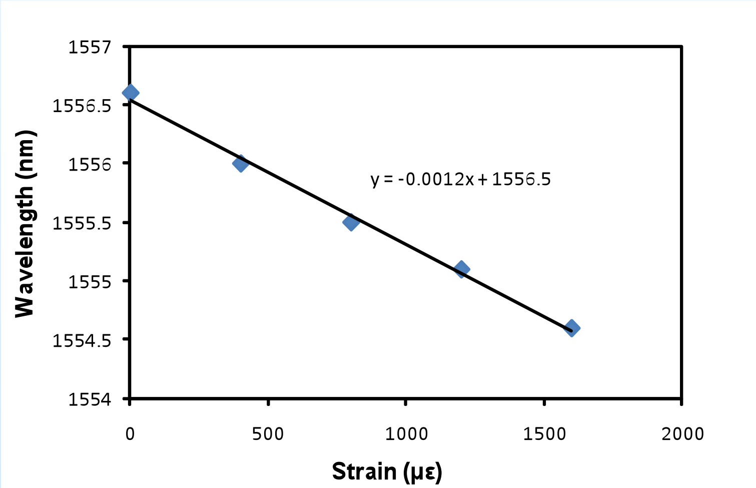


LP06-Taper Coupler

Side Coupled Tapers







Interferometer behavior

Spectral shift as a function of the overlapping length

3.2 Development of Sensing Materials

— Proton Conducting Perovskite Oxides

- Selection of Proton Conducting Perovskite Oxides:
  - **Cerate-based:** higher sensitivity, low stability in CO_2
  - **Zirconate-based:** higher stability in CO_2, lower sensitivity
- Four perovskite materials synthesized and tested
  - $Sr(Ce_{0.8}Zr_{0.1})Y_{0.1}O_{2.95}$ (SCZY)
  - $SrCe_{0.95}Tm_{0.05}O_{3-a}$ (SCTm)
  - $SrCe_{0.95}Tb_{0.05}O_{3-a}$ (SCTb)
  - $SrZr_{0.95}Y_{0.05}O_{3-a}$ (SZY)
- General observations
  - All four materials are functional for H_2 detection
  - Moderately higher sensitivity for cerate-based (SCTm and SCTb)
- Stability in simulated gases will be evaluated in Year-2

Perovskite Reaction with Gases

- **Gas-induced changes in defect type and population, electron states and band gap energy, lattice parameters, and density of the oxide alter the electric conductivity and optical properties (e.g. refractive index).**

High temperature gas-solid reactions:

$$V_O^{\bullet\bullet} + \tfrac{1}{2}O_2 \xleftrightarrow{k_1} O_O^X + 2h^{\bullet}$$

$$[h^{\bullet}] = \sqrt{k_1} P_{O2}^{1/4} [V_O^{\bullet\bullet}]^{1/2} [O_O^X]^{-1/2}$$

$$H_2 + 2h^{\bullet} + O_O^X \xleftrightarrow{k_2} 2OH^{\bullet}$$

$$[OH^{\bullet}] = \sqrt{k_2} P_{H2}^{1/2} [h^{\bullet}][O_O^X]^{1/2}$$

$$H_2 + 2O_O^X \xleftrightarrow{k_3} 2OH^{\bullet} + 2e^-$$

$$[OH^{\bullet}]n = \sqrt{k_3} P_{H2}^{1/2} [O_O^X]$$

$$O_O^X \xrightarrow{Red.} \tfrac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e^-$$

$$H_2O + V_O^{\bullet\bullet} + O_O^X \longleftrightarrow 2OH^{\bullet}$$

$$H_2S + V_O^{\bullet\bullet} + 2O_O^X \longleftrightarrow 2OH^{\bullet} + S_{(S)}$$

Possible Interferences by H2S, CO, CH4 etc., which were found to be insignificant at 500°C

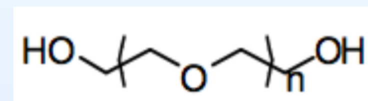
Procedure of Thin Film Coating

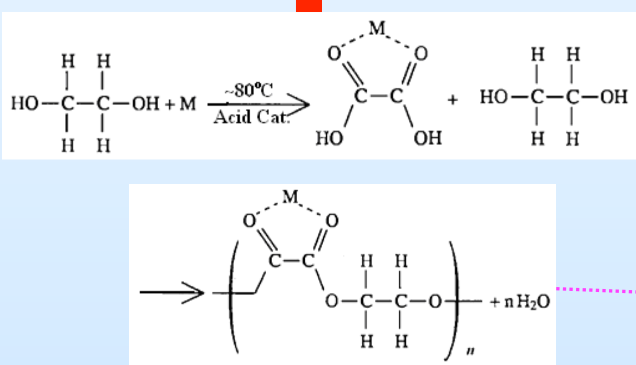
EXAMPLE: $Sr(Ce_{0.8}Zr_{0.1})Y_{0.1}O_{2.95}$ (SCZY) nano-film synthesis

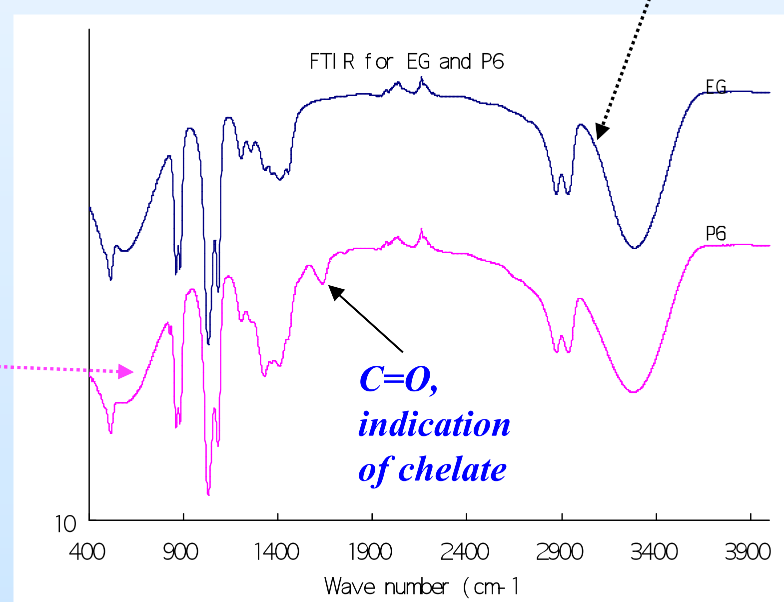
STEP 1
Polymeric precursor synthesis: $Sr^{2+}/Zr^{4+}/Ce^{4+}/Y^{3+}$ PEG chelate by acid catalyzed polymerization

STEP 2
Precursor film coating: Brush-coating polymeric precursor film on LPFG surface and drying

STEP 3
CDZ nanocrystalline film: conversion of precursor film to solid oxide film by firing/annealing

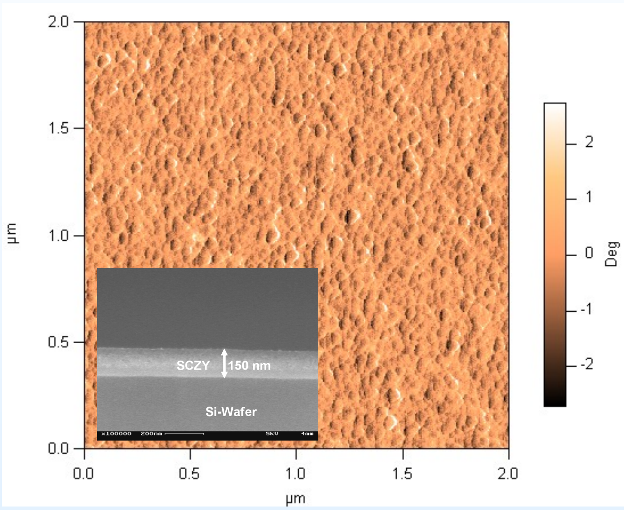




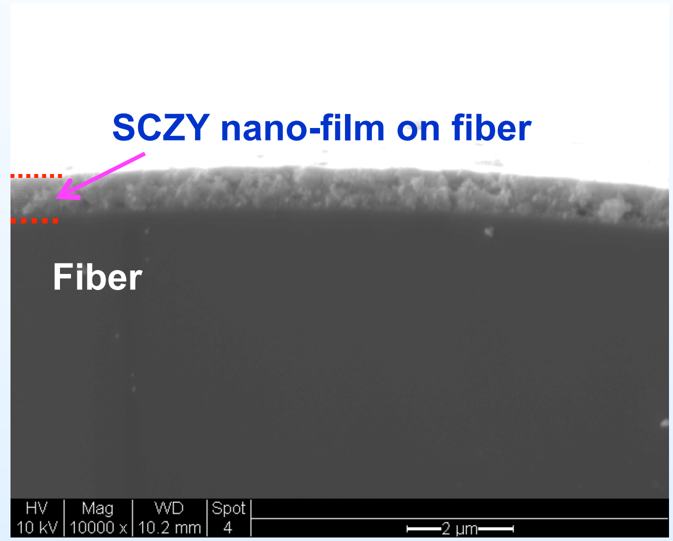


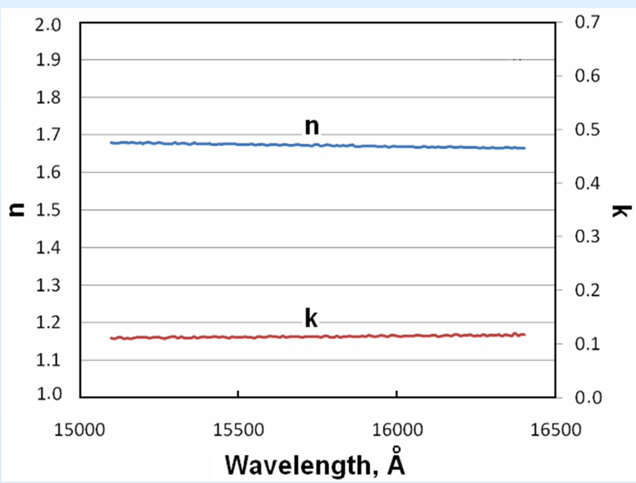
M = Sr, Zr, Ce, Y

Typical Microstructure and Index of Nanofilm

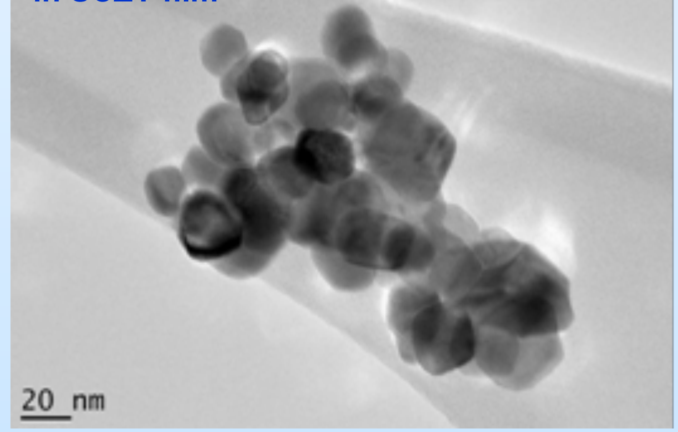


The surface (AFM) and cross-section (SEM) of SCZY film on Si



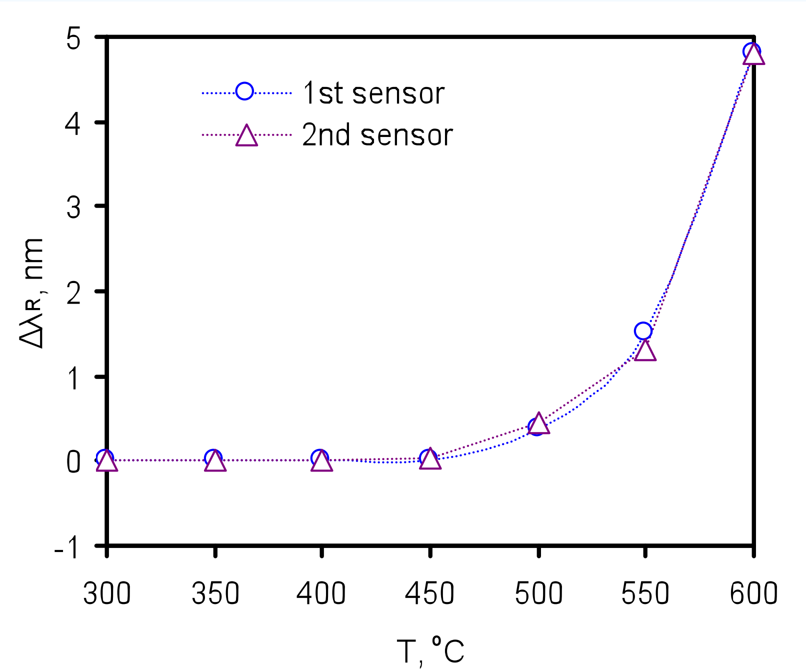


Refractive index (n) and extinction constant (k) by ellipsometry

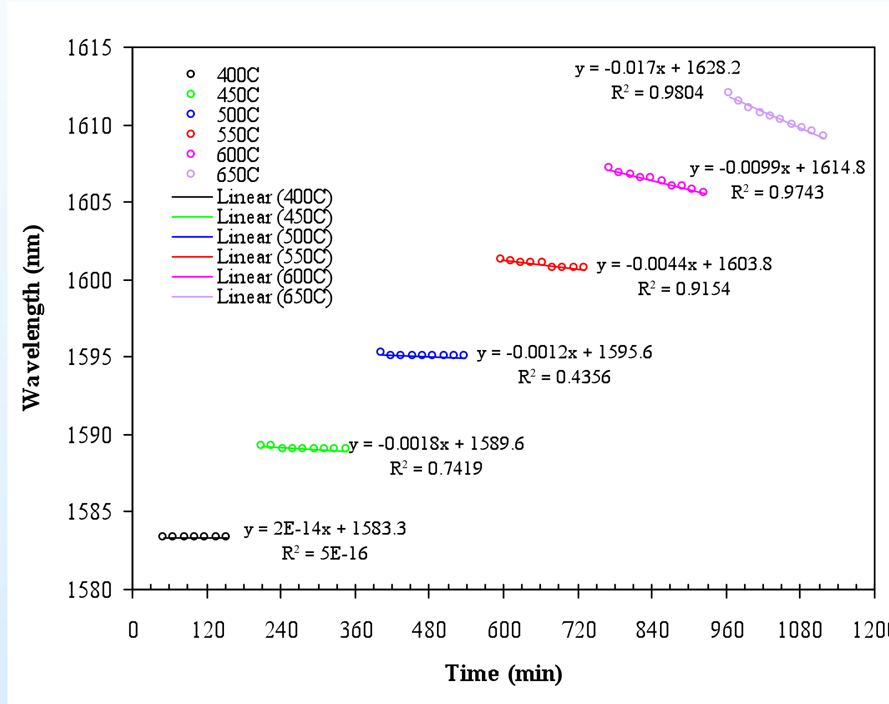


Morphology of nano-grains in SCZY film

Effect of Operation Temperature on H_2 Sensitivity and Sensor Stability



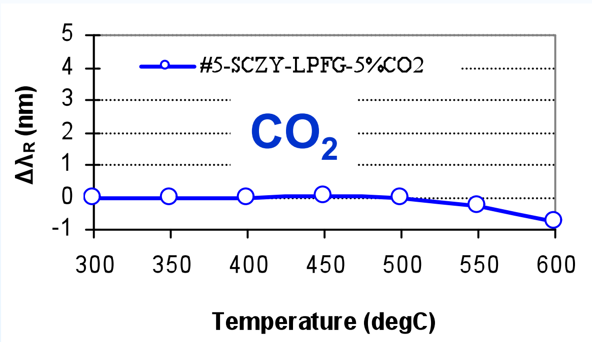
Response of the SCZY-LPFG to 5% H_2 in N_2 as a function of temperature



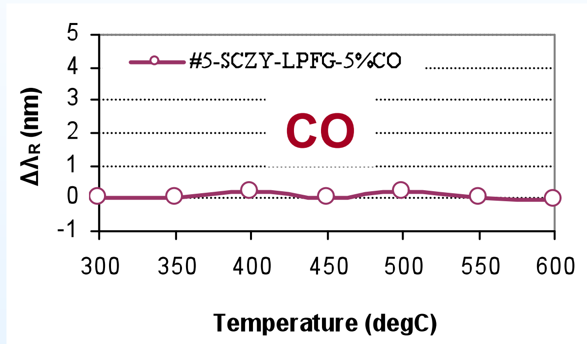
SCZY-LPFG thermal drift at different temperatures

Increasing temperature provides higher sensitivity by lowers stability

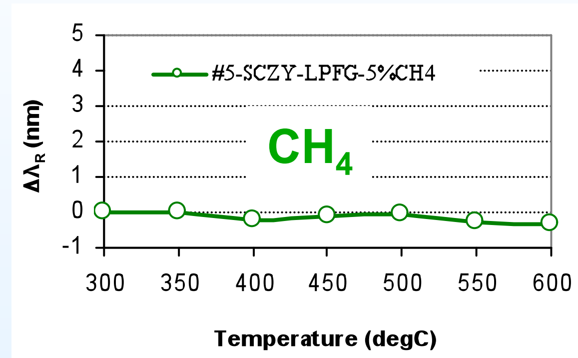
Effect of Operation Temperature on Interference from Other Gases in H_2 Detection



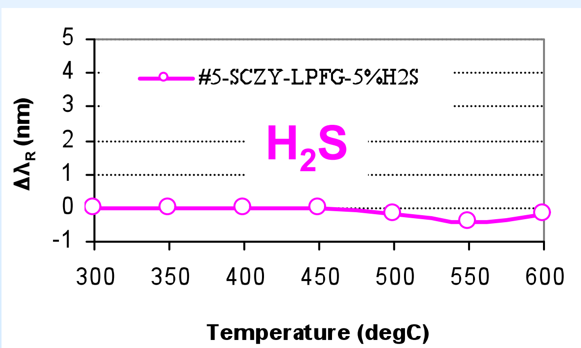
Response of the SCZY-LPFG to 5% CO_2 in N_2 vs. temperature



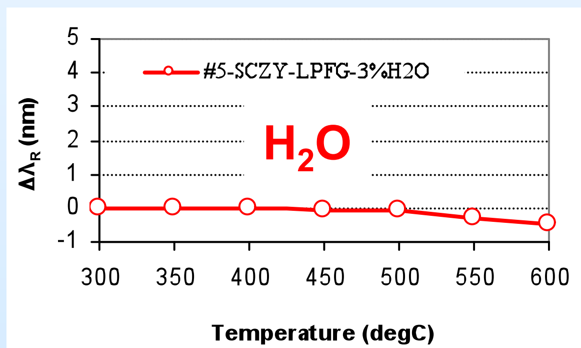
Response of the SCZY-LPFG to 5% CO in N_2 vs. temperature



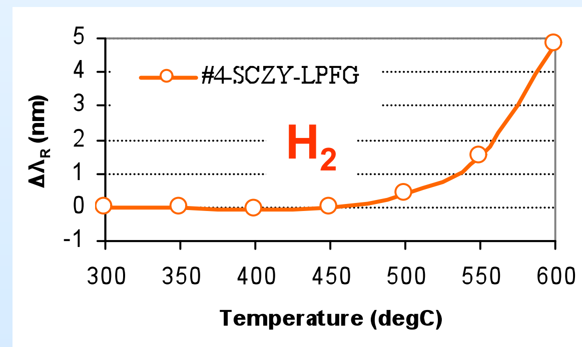
Response of the SCZY-LPFG to 5% CH_4 in N_2 vs. temperature



Response of the SCZY-LPFG to 5% H_2S in N_2 vs. temperature



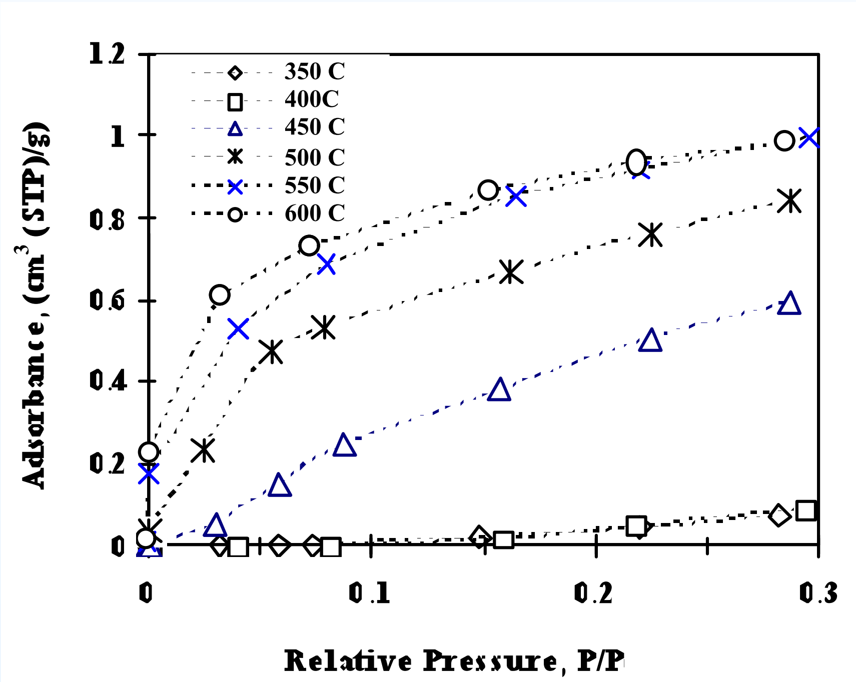
Response of the SCZY-LPFG to 3% H_2O in N_2 vs. temperature



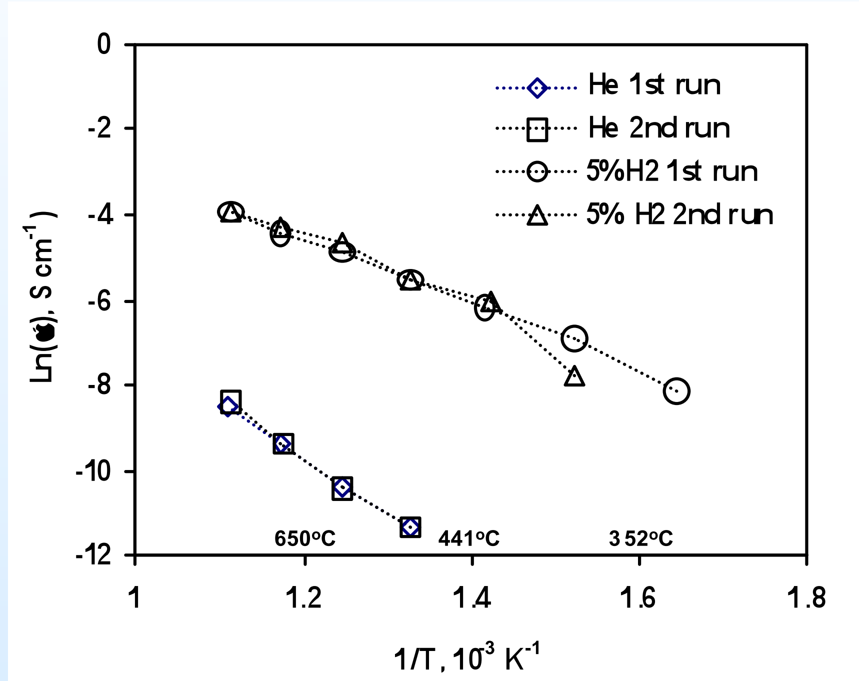
Response of the SCZY-LPFG to 5% H_2 in N_2 vs. temperature

Compared to the Interferences from H_2O, CO_2, H_2S, CO, and CH_4 are insignificant at temperatures up to 500 °C; the interferences from these gases (except for CO) increase with temperature at > 550°C; Thus, operating at 500 oC also minimizes the interferences for measurement of H2 in coal-derived syngas.

Effect of Operation Temperature on H_2 Sorption and Electric Conductivity of SCZY



Hydrogen uptake in SCZY nanoparticles at difference temperatures



Total electric conductivity of the SCZY film as a function of temperature in 5% H_2 and pure helium

3.1 Development of Sensing Materials
— Copper-Doped-Zirconia (CDZ)

- **Materials synthesized and tested**
  - CDZ (0% Cu; i.e. pure zirconia)
  - CDZ (3% Cu)
  - CDZ (8% Cu)
  - CDZ (16% Cu)
- **General observations**
  - Pure ZrO_2: very low sensitivity (small response in DI_R)
  - High Cu-content: high sensitivity but low stability due to over reduction to form Cu^0 which segregates irreversibly to grain boundaries in the film.
  - Low Cu content: large measuring range but low sensitivity for low-concentration CO detection.

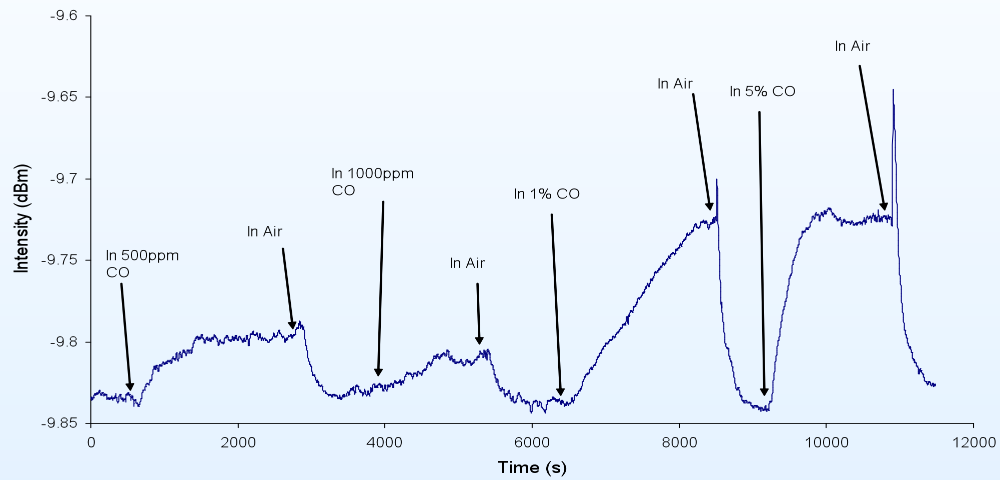
3.1 Development of Sensing Materials
— Copper-Doped Zirconia for CO Detection

Small response by ZrO_2-LPFG:

$$ZrO_2 + CO \rightarrow ZrO_{2-\delta} + CO_2$$

Reverse reaction in O_2:

$$ZrO_{2-\delta} + O_2 \rightarrow ZrO_2$$



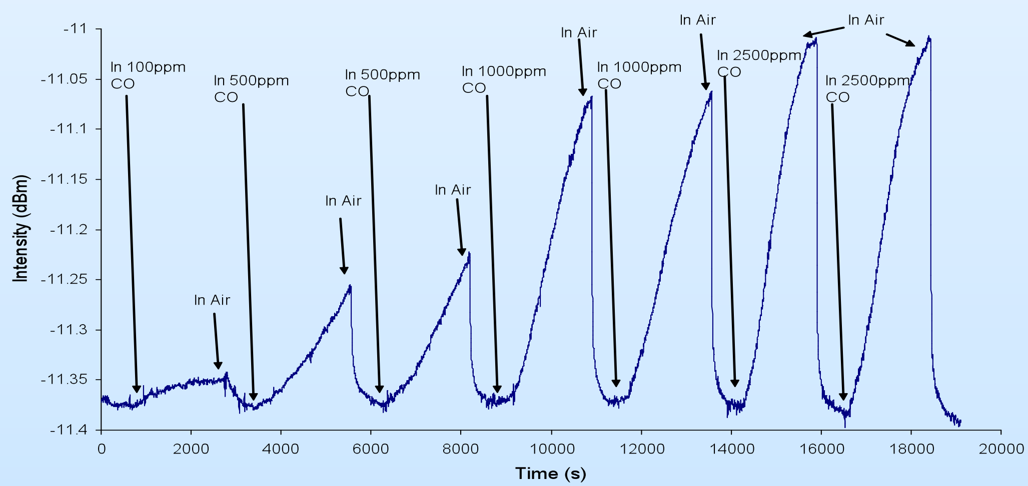
Pure Zirconia (0%)

Enhanced response by Cu dopant:

$$CuO + CO \rightarrow Cu_2O + CO_2$$

Reverse reaction in O_2:

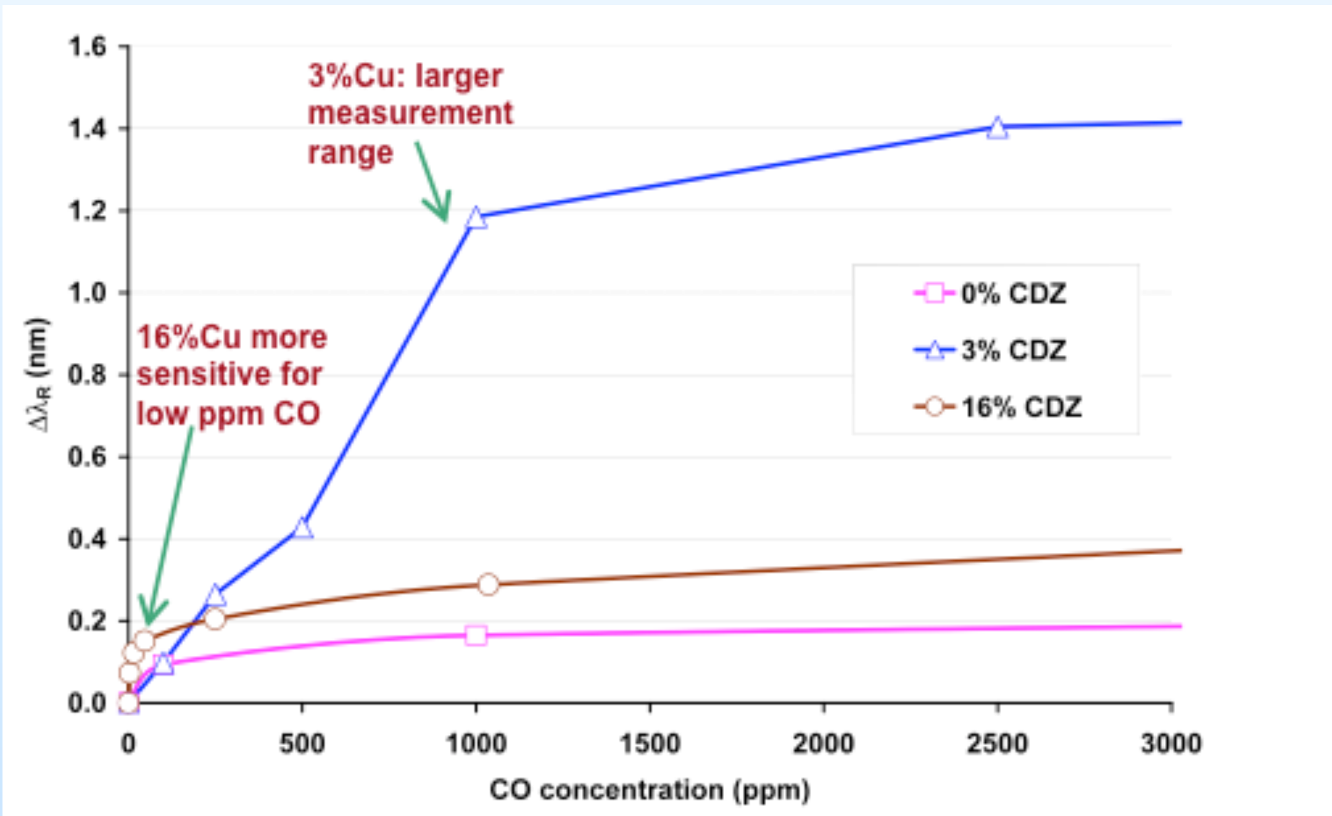
$$Cu_2O + \tfrac{1}{2}O_2 \rightarrow 2CuO$$



Copper-doped Zirconia (3%Cu)

CDZ-LPFG: DI_R as a function of CO concentration at 550°C and 1 atm – effect of Cu content

- Pure ZrO2: very low sensitivity (small response in DIR)
- High Cu-content: high sensitivity; low stability due to Cu^0 formation
- Low Cu content: large measuring range; low sensitivity for low-concentration CO



4. Summary of Work Done

- **Design, fabrication and preliminary test of the two types of fiber devices:**
  - Extensively studied the device physics of the two proposed sensor platforms
  - Preliminarily evaluated the device performance in high temperature environment
  - Developed strategies for temperature compensation and multiparameter measurement
  - Derived device design guidelines
- **Proton conducting perovskite oxide film synthesis, characterization, and study for H_2 sensing**
  - Developed procedures for the synthesis of four perovskite oxide thin films;
  - Studied the H_2 sorption and electrical conductivity as functions of temperature;
  - Investigated the effect of temperature on H_2 sensitivity, thermal drifting, interferences of other gases for the SCZY-LPFG;
  - 500^{o}C is the desirable operation temperature to minimize the thermal instability and avoid interferences from co-existing gases, although higher temperature offers higher sensitivity.
- **Copper doped zirconia (CDZ) film synthesis and study for CO sensing**
  - CDZ nanofilms with various Cu content (0 ~ 16%) were synthesized on LPFG;
  - The CO detection sensitivity (at 550^{o}C) in creases with increasing Cu content;
  - The stability of the CDZ film decreases with increasing Cu content (material instability caused by over reduction of Cu^{2+} to copper metal, i.e. Cu^{0});
  - Lower Cu content allows for wider measuring range for CO (with higher up limit)
  - CDZ-LPFG is well suited for low concentration CO monitoring, e.g. combustion exhaust …

5. Work Plan for Year-2 (Phase-II)

- **Task 3.0:** Fabricate the LPFG-coupled interferometer and evanescent tunneling fiber sensors and conduct extensive characterizations on doped-ceramic materials and microstructures of the nanofilms.
  - **Subtask 3.1** (Xiao MST) Fabricate the LPFG-coupled interferometer and evanescent tunneling fiber devices using an existing CO_2-laser fabrication process.
  - **Subtask 3.2** (Dong, UC) Examine the properties of the material for sensor application and optimize the composition and crystallite size of the ceramic materials.
  - **Subtask 3.3** (Dong, UC) Synthesize doped-ceramic nanofilms on structured fibers and optimize the grain size, thickness, and density to enhance the sensor performance.
  - **Subtask 3.4** (Xiao/MST and Dong/UC) Test the optical sensors for binary gas mixtures containing N_2 and a target gas at high temperatures with and without water vapor.

Appendix: Publications

- ***Peer-reviewed journal papers:***

1. X. Tang, K. Remmel, X. Lan, J. Deng, H. Xiao, J. Dong, Perovskite-Type Oxide Thin Film Integrated Fiber Optic Device for High Temperature Hydrogen Measurement. *Analytical Chemistry* 81 (2009) 7844-7848.
2. Y. Zhang, Y. Li, T. Wei, X. Lan, Y. Huang, G. Chen, H. Xiao, "Fringe Visibility Enhanced Extrinsic Fabry-Perot Interferometer Using a Graded Index Fiber Collimator," IEEE Photonics Journal, 2010, doi: 10.1109/JPHOT.2010.2049833
3. X. Tang, Z. Xu, S.-J. Kim, J. Dong, H. Duan, H. Xiao, Gas Sensing by Zeolite Coated Fiber Optical Device Based on Selective Molecular Adsorption. *Langmuir* (2010) ***submitted.***

- ***Conference papers/presentations:***

1. Y. Zhang, X. Lan, T. Wei, H. Duan, H. Xiao, Side-coupled optical fiber devices for sensing applications. *SPIE Symp. on Defense, Security + Sensing*, Orlando, FL, USA, Apr. 5-9, 2010.
2. X. Tang, Z. Xu, J. Dong, H. Duan, H. Xiao, Development of Nanocrystalline Thin Films of Proton Conducting Perovskite Oxides for High Temperature H_2 Separation and Optical Probing in Fossil Fuel Gases. *AIChE Annual Meetg.*, Salt Lake City, UT, USA, Nov. 7 -12, 2010.
3. X. Tang, K. Remmel, D. Sandker, Z. Xu, J. Dong, Proton Conducting Perovskite-Type Ceramics for Fiber Optic Sensors for Hydrogen Monitoring at High Temperature. *SPIE Symposium on Defense, Security + Sensing*, Orlando, FL, USA, Apr. 5-9, 2010.
4. Hongbiao Duan, Xinwei Lan, Tao Wei, Yinan Zhang and Hai Xiao, Characteristics and application of phase-shifted long-period fiber grating fabricated by CO2 laser. *SPIE Symposium on Defense, Security + Sensing*, Orlando, FL, USA, Apr. 5-9, 2010.
5. J. Dong, X. Tang, K. Remmel, H. Xiao, Nanostructured Inorganic Thin Film Enabled Fiber Optic Sensors for Gas Sensing in Energy and Environmental Systems, *MS&T Conference*, Pittsburgh PA, Oct. 2009.